Non-resonant driving of H atom with broken time-reversal symmetry

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The dynamics of atomic hydrogen placed in a static electric field and illuminated by elliptically polarized microwaves is studied in the range of small field amplitudes where perturbation calculations are applicable. For a general configuration of the fields any generalized time-reversal symmetry is broken and, as the classical dynamics is chaotic, the level statistics obeys the random matrices prediction of Gaussian unitary ensemble.

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The Bohigas, Giannoni and Schmit conjecture [1] that a general quantum system with underlying chaotic classical dynamics has statistical properties of energy levels described by random matrices theory has been confirmed by theoretical studies of numerous chaotic systems, see e.g. [2,3]. Experimental verifications on the other hand are much less abundant [4,5] and, as far as we know, concern only systems possessing anti-unitary (generalized time-reversal) symmetry where the level statistics can be modeled by random matrices of the Gaussian orthogonal ensemble (GOE) [6]. Realization of a quantum system with quadratic level repulsion as is typical for matrices from the Gaussian unitary ensemble (GUE) [6] requires breaking of any anti-unitary symmetry invariance. E.g. for atomic or molecular systems it means one would have to apply magnetic field inhomogeneous across the molecule being well experimentally controlled on such a small scale [2]. Such a requirement is rather unattainable even in the Rydberg regime of excitation. While a real quantum system with GUE statistics has not been realized experimentally, there are experiments with microwave cavities (so-called *wave chaos* experiments) where anti-unitary symmetry can be broken by applying some ferrite devices [7,8].

Recently, however, it has been shown [9,10] that to break anti-unitary symmetry invariance, in atomic systems, it is not necessary to employ magnetic field. Indeed a combination of elliptically polarized microwaves with a static electric field applied to, e.g., hydrogen (H) atoms can do this work as well. In the previous studies [9,10] we have restricted ourselves to a case when the microwave field is resonant with the classical motion of the electron, i.e. the ratio of microwave frequency, ω, to Kepler frequency, $\omega_K = 1/n_0^3$ (where n_0 is the principal quantum number of H atom), is an integer number. It has been found that such a system can reflect level statistics very close to the GUE prediction.

In this paper we study a more general situation of non-resonant driving of the atoms and show that appropriate choice of the system parameters allows us to reach statistical properties expected for matrices of the GUE. We consider weak fields limit where quantum results may be obtained by the lowest orders of the perturbation theory. Classical investigation of the system behavior is carried out also in terms of the perturbation calculations. It allows us to find out for which system parameters the secular motion of the electronic ellipse reveals chaotic dynamics.

The Hamiltonian of a realistic three-dimensional H atom placed in a static electric field and driven by an elliptically polarized microwave field in atomic units, neglecting relativistic effects, assuming infinite mass of the nucleus, and employing dipole approximation reads:

$$H = \frac{\mathbf{p^2}}{2} - \frac{1}{r} + F(x\cos\omega t + \alpha y \sin\omega t) + \mathbf{E}\cdot\mathbf{r}, \qquad (1)$$

where F, α and ω are, respectively, the amplitude, degree of elliptical polarization and frequency of the microwave field while $\mathbf{E}$ stands for the static electric field vector. As the external perturbation is time periodic, one may apply Floquet formalism and look for quasienergy levels of the system.

We assume very small field amplitudes which allows including only the lowest non-vanishing terms in the quantum effective Hamiltonian [11] describing the dynamics of a given n_0 hydrogenic manifold. The static electric field contributes already in the first order of E as the states with fixed n_0 are coupled among each other by the $\mathbf{E}\cdot\mathbf{r}$ operator. On the other hand there is no *direct* coupling between the states due to the microwave perturbation. Indeed the states can be coupled only *indirectly* by the process of absorption and emission of microwave photons. So that the first non-vanishing term is second order in F. The final matrix (with n_0^2 dimension) of the quantum effective Hamiltonian, i.e. the Hamiltonian in the first order in E and second order in F, is then diagonalized by standard routines. The details of the quantum perturbation calculations can be found in [10], here we would only like to stress that the whole physically realistic problem is reduced to the analysis of the finite n_0^2 dimensional Hilbert space where $1/n_0$ plays the rôle of the effective Planck constant.

We are now turning to classical analysis of the system. The range of our interests is the high frequency regime, i.e. $\omega > \omega_K$, which means that for weak external fields we have two fast degrees of freedom in the system, i.e.

the position of the electron on an elliptical orbit and the phase of the microwave field, and two slow degrees of freedom corresponding to the orientation of the elliptical trajectory. One can get rid of the fast degrees of freedom by means of the classical perturbation theory [12] which results in the classical effective Hamiltonian describing slow precession of an electronic ellipse. The perturbation calculation can be easily carried out employing the Lie method [12], actually it closely follows the similar procedure applied in [13] to the H atom perturbed by linearly polarized microwave field. The first stage is to express the Hamiltonian (1) in terms of the action-angle variables of the unperturbed hydrogen atom. The new pairs of the canonically conjugate variables are (J, Θ), i.e. principal action (analog of the principal quantum number, n_0) and position of the electron on an ellipse respectively; (L, Ψ), i.e. angular momentum of the electron and conjugate angle; and finally (M, Φ), i.e. angular momentum projection on z axis and angle of rotation around this axis [14]. Averaging the resulting Hamiltonian over Θ and t immediately gives the first order contribution to the classical effective Hamiltonian

$$\begin{aligned} H^{(1)}(L,\Psi,M,\Phi) = &-\frac{3}{2}n_0^2\sqrt{1-\frac{L^2}{n_0^2}} \\ &\left[E_x\left(\cos\Phi\cos\Psi - \frac{M}{L}\sin\Phi\sin\Psi\right)\right. \\ &+E_y\left(\sin\Phi\cos\Psi + \frac{M}{L}\cos\Phi\sin\Psi\right) \\ &\left.+E_z\sqrt{1-\frac{M^2}{L^2}}\sin\Psi\right]. \end{aligned} \tag{2}$$

The second order contribution of microwave field requires calculating the generating function, w [12] which is the solution of the following equation

$$\frac{\partial w}{\partial t} + \omega_K\frac{\partial w}{\partial \Theta} = -H_{micro}, \tag{3}$$

where H_{micro} is the microwave part of the Hamiltonian (1) expressed in the action-angle variables (explicit expression for H_{micro} as a Fourier series can be found in [14]). The solution for w is given as an infinite series with terms containing $1/(\omega \pm m\omega_K)$, where m is an integer number. For resonant driving, i.e. $\omega/\omega_K \approx m$, one faces the small denominators problem [12] but here we are not affected by this problem as we are interested in a non-resonant perturbation. Having calculated w it is straightforward task to obtain the second order contribution to the effective Hamiltonian by averaging the Poisson bracket of w and H_{micro} over Θ and t, i.e.

$$H^{(2)}(L,\Psi,M,\Phi) = \frac{1}{2}\langle\{w, H_{micro}\}\rangle_{\Theta,t}, \tag{4}$$

(we omit the lengthy explicit formula for $H^{(2)}$ here). The final classical effective Hamiltonian reads

$$H^{eff}(L,\Psi,M,\Phi) = -\frac{1}{2n_0^2} + H^{(1)} + H^{(2)}. \tag{5}$$

This is the classical counterpart of the quantum effective Hamiltonian, namely first order in the static electric field and second order in microwave field. The classical Hamiltonian (5) possesses scaling symmetry, i.e. one can get rid of one of the parameters of the system. Introducing $F_0 = n_0^4F$, $E_0 = n_0^4E$, $\omega_0 = n_0^3\omega$, $L_0 = L/n_0$, $M_0 = M/n_0$ and $H_0^{eff} = n_0^2H^{eff}$ the dynamics becomes independent of the particular choice of the n_0 hydrogenic manifold.

For a general fields configuration the secular motion in the (L, Ψ, M, Φ) phase space is not integrable and to investigate classical dynamics we have to perform numerical integration of the equations of motion generated by the Hamiltonian (5). For the linear microwave polarization without additional static electric field considered in [13] the secular motion was one dimensional and employing the WKB quantization rule [2] the authors were able to get semiclassical predictions for quasienergy levels in a very good agreement with exact quantum numerical data.

For elliptically polarized microwaves and general orientation of the static field vector the anti-unitary symmetry invariance is broken. Only when either $E_x = 0$ or $E_y = 0$ the system is invariant with respect to the time-reversal combined with $x \to -x$ or $y \to -y$ transformations respectively, see (1). As an example of a general elliptical polarization case we have further on analyzed the degree of the polarization $\alpha = 0.4$. The microwave frequency has been chosen as $\omega_0 = 1.304$ and the amplitude as $F_0 = 0.02$ which is well in the range where, for the linear microwave polarization, the WKB calculations give good agreement with the exact numerical results [13]. Then by investigating Poincaré surface of section we have found that the amplitude $E_0 = 0.00028$ and the orientation of the static field vector $\phi \approx 0.3\pi$, $\theta \approx \pi/4$ (where θ, ϕ are usual spherical angles) correspond to chaotic dynamics in the energy interval $H_0^{eff} \in [-0.50032, -0.50008]$. Putting $\phi = 0$ ($E_y = 0$) one recovers anti-unitary symmetry of the system, then the classical dynamics is found to be predominately chaotic for $H_0^{eff} \in [-0.50016, -0.49992]$. Fig. 1 shows examples of the phase space structures for both $\phi = 0$ and $\phi = 0.3\pi$.

Having done classical analysis we can switch to quantum calculation results. In order to get reasonable statistics for quasienergy levels we have diagonalized the matrix of the quantum effective Hamiltonian for different n_0 manifolds in the range $n_0 = 50 \div 59$. From each diagonalization we have separated and unfolded spectrum in the energy intervals corresponding to chaotic classical dynamics. This procedure has been applied to the anti-unitary invariant case ($\phi = 0$) and to the case with broken anti-unitary symmetry ($\phi = 0.3\pi$). Fig. 2 shows histograms of the nearest neighbor spacing (NNS) distributions of the quasienergy levels (there are about 10^4

spacings in each of the data sets) together with the plots of the Wigner surmises [3] for the GOE and GUE. The figure also shows the spectral rigidities, i.e. Δ_3 statistics [3]. The qualitative agreement of the data with the random matrices theory is apparent, especially for the case with broken anti-unitary symmetry.

To focus on quantitative measure we have fitted theoretical NNS distributions to the data (to avoid the dependence of the results on bin size the distributions have been fitted to the cumulative histograms [15]). For the anti-unitary invariant case the best fitting Berry-Robnik distribution (i.e. the distribution for independent superposition of Poisson and GOE spectra [16]) results in the parameter value (relative measure of the chaotic part of the phase space) $q = 0.98$ with $\chi^2/N = 0.3$, i.e. chi-squares divided by the number of spacings N. Employing the Izrailev distribution [17,18] we get the value of the levels repulsion parameter $\beta = 0.96$ with $\chi^2/N = 0.8$. For the spectral rigidity the best fitting Δ_3 statistics corresponding to an independent superposition of Poisson and GOE spectra [3] results in $q = 0.99$ which is in agreement with the value obtained from the Berry-Robnik distribution fit.

In the case with broken anti-unitary symmetry one gets the following parameters values: Berry-Robnik statistics (now it corresponds to independent superposition of the Poisson and GUE spectra [19]) $q = 1$ with $\chi^2/N = 0.2$, Izrailev distribution $\beta = 2.05$ with $\chi^2/N = 0.3$ and from the spectral rigidity fit $q = 1$.

The presented results show undoubtedly that the system under consideration can reflect the Bohigas, Giannoni and Schmit conjecture both with or without anti-unitary symmetry. The question is if such a behavior can be observed experimentally? With this respect let us consider the case with broken generalized time-reversal symmetry. As there is no discrete symmetry in the system one has no problems with separation of overlapping spectra. On the other hand it results in a big density of states and requires high experimental resolution. We have presented the data for hydrogenic manifolds in the range $n_0 = 50 \div 59$ in order to have good statistics but our results for $n_0 = 40 \div 49$ reveal the very same behavior. For example for $n_0 = 40$ and $F = 40$ V/cm, $\omega = 2\pi \cdot 134$ GHz, $E = 0.56$ V/cm the average level spacing is of order 10^{-4} cm^{-1} and a measurement in the energy range between -68.628 cm^{-1} and -68.595 cm^{-1} provides about 500 levels. It sounds feasible experimentally.

The previous studies [9,10] have been devoted to resonant microwave driving of H atoms placed in a static electric field. The present work deals with a general non-resonant driving and shows that intra-manifold chaotic dynamics [20–22,9,10], i.e. the situation when states corresponding to a fixed principal quantum number n_0 are mixed significantly only among each other and underlying classical dynamics is irregular, is not restricted to a particular resonant case but exists widely in the frequency domain. The presented behavior is field amplitudes independent, i.e. if $F \to 0$ and $E \to 0$ but $E/F^2 = const$ the structure of the phase space corresponding to secular motion remains unchanged as are the statistical properties of quasienergy levels. This is a signature of inapplicability of the Kolmogorov-Arnold-Moser theorem [12] to a highly degenerate Coulomb problem. For high field amplitudes when hydrogenic manifolds can not be considered isolated and the inter-manifold mixing comes to the scene our perturbation approach, obviously, becomes irrelevant. However this regime, for a realistic three-dimensional problem, still constitutes a challenge for the theory.

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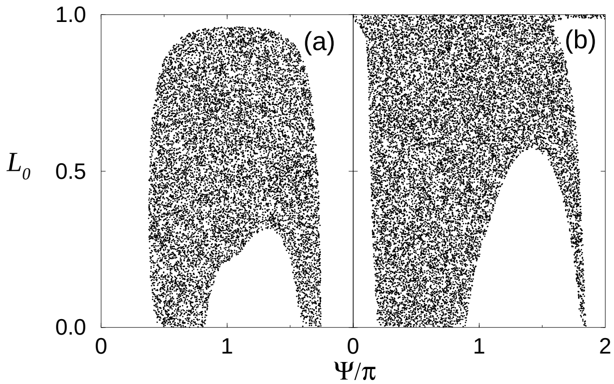

FIG. 1. Poincaré surface of section (at $\Phi = 0$) of the classical secular motion, Eq. (5), for the hydrogen atom placed in a static electric field, with the amplitude $E_0 = 0.00028$, and driven by an elliptically polarized ($\alpha = 0.4$) microwave field with frequency $\omega_0 = 1.304$ and amplitude $F_0 = 0.02$. The coordinates used for the plot are the scaled angular momentum $L_0 = L/n_0$ and its canonically conjugate angle Ψ. Panel (a) corresponds to the anti-unitary invariant case, i.e. the orientation of static field vector is $\phi = 0$, $\psi = \pi/4$; with the energy $H_0^{eff} = -0.50008$. Panel (b) is related to the broken anti-unitary invariance, i.e. $\phi = 0.3\pi$, $\psi = \pi/4$; with the energy $H_0^{eff} = -0.5002$. Note that, for the parameters chosen, not the whole (L_0, ψ) space is accessible.

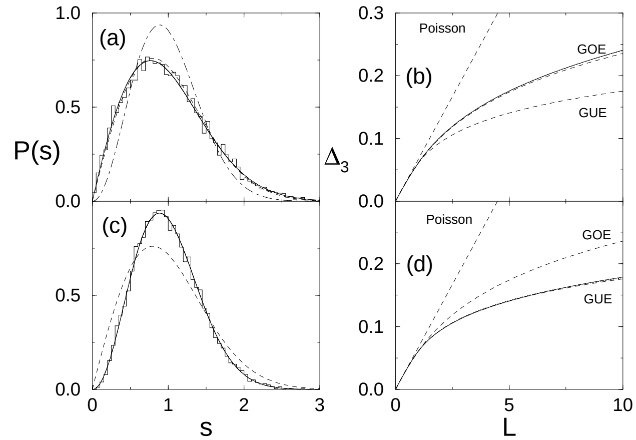

FIG. 2. Nearest neighbor spacing distribution and spectral rigidity, Δ_3 statistics, for hydrogen atom placed in a static electric field and illuminated by microwave field, for the case with [panels (a)-(b)] and without [panels (c)-(d)] anti-unitary symmetry invariance, compared with predictions of random matrices ensembles. The data have been collected for $n_0 = 50 \div 59$ with the same fields parameters as in Fig. 1. In panels (a) and (c) solid lines indicate the best fitting Izrailev distributions, while dashed and dash-dotted lines correspond to GOE and GUE distributions respectively (in panel (c) the dash-dotted line is invisible behind the solid one). Panels (b) and (d): solid and dotted (hardly visible behind the solid lines) lines correspond to numerical data and their best fits, while dashed lines indicate Poisson, GOE and GUE predictions as indicated in the figure.